REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
09-08-2011	Final	April 1, 2007- March 31, 2010

4. TITLE AND SUBTITLE
Dislocation Diffusion in Metallic Materials

5a. CONTRACT NUMBER
FA9550-07-1-0240

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
George Mason University
Department of Physics and Astronomy
Fairfax VA 22030

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR
875 N Randolph
Arlington VA 22203

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-OSR-VA-TR-2013-0992

12. DISTRIBUTION/AVAILABILITY STATEMENT
Distribution A

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The goals of this project were: (1) perform a fundamental study of atomic diffusion along dislocation cores in metals and alloys, (2) develop new methods for the calculation of dislocation diffusion coefficients as functions of temperature and chemical composition and (3) calculate diffusion rates along screw, edge and mixed dislocations in Al and Al alloys. To achieve these goals a new interatomic potential for Al-alloy system need to be developed and tested against a large database of experimental and first principles data. Monte carlo and molecular dynamics simulations were performed to determine the atomic mechanisms of dislocation diffusion and their dependence on temperature and alloying. The new methodologies will be applicable to other classes of materials relevant to the Air Force mission.

15. SUBJECT TERMS
Al-alloy, Monte Carlo, molecular, dynamics and atomic

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			David Stargel
					19b. TELEPHONE NUMBER *(Include area code)* 703-696-6961

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DISLOCATION DIFFUSION IN METALLIC MATERIALS
AFOSR GRANT NUMBER FA9550-07-1-0240

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FINAL PERFORMANCE REPORT

Abstract

The goals of this project were: (1) perform a fundamental study of atomic diffusion along dislocation cores in metals and alloys, (2) develop new methods for the calculation of dislocation diffusion coefficients as functions of temperature and chemical composition, and (3) calculate diffusion rates along screw, edge and mixed dislocations in Al and Al alloys. To achieve these goals, a new interatomic potential for an Al-alloy system needed to be developed and tested against a large database of experimental and first-principles data. Monte Carlo and molecular dynamics (MD) simulations were performed to determine the atomic mechanisms of dislocation diffusion and their dependence on temperature and alloying. The new methodologies will be applicable to other classes of materials relevant to the Air Force mission. This report covers performance period from April 1 2007 to March 31, 2010.

Technical approach and results

Atomic diffusion along lattice dislocations plays a critical role in many processes in metallic materials, such as dynamic strain ageing (DSA), nucleation and coarsening of disperse particles in precipitation-hardened alloys, creep, sintering, and mechanical alloying. The dislocation diffusion coefficient D_d is the key physical parameter in many models of materials behavior during processing, fabrication and service. Reliable experimental measurements of dislocation diffusion coefficients require radioactive isotopes and are extremely difficult and expensive, not to mention the environmental and safely concerns. Theory, modeling and computer simulations offer the most efficient way of gaining insights into the mechanisms of dislocation diffusion and for making reliable predictions of dislocation diffusion coefficients. As model systems, we chose pure Al and Al-Cu alloys as prototypes of commercial Al-based alloys used in Air Force applications. The approach was to first study dislocation diffusion in pure Al. Once the basic atomic mechanisms are understood and the methodology is established, the effect of Cu segregation on dislocation diffusion would be studied using the new interatomic potential which was developed in this project.

We have studied self-diffusion along pure screw and edge dislocations in Al using MD simulations with the embedded-atom potential for Al developed by the PI previously [Y. Mishin et al, *Phys. Rev.* B **59**, 3393 (1999)]. Each dislocation is found to slightly dissociate into 1/6

<211> Shockley partials on a {111} plane. To assess the strength of interactions of the dislocations with point defects, the vacancy and interstitial formation energies have been computed in the vicinity of the core by the molecular statics method (Figure 1). In the core regions, the vacancy formation energy is reduced relative to the perfect lattice region by almost 0.15 eV. The effect of the edge dislocation on the vacancy formation energy is greater and extends over a larger area in comparison with the screw. For the edge dislocation, the contour plots of the vacancy formation energy closely correlate with the elastic tension-compression fields around the core. The effect of the dislocations on the interstitial formation energy is greater but much more localized on the core. Using the point-defect formation energies E, their equilibrium concentrations c in the core region have been calculated from the standard Boltzmann relation $c = \exp(-E/k_BT)$.

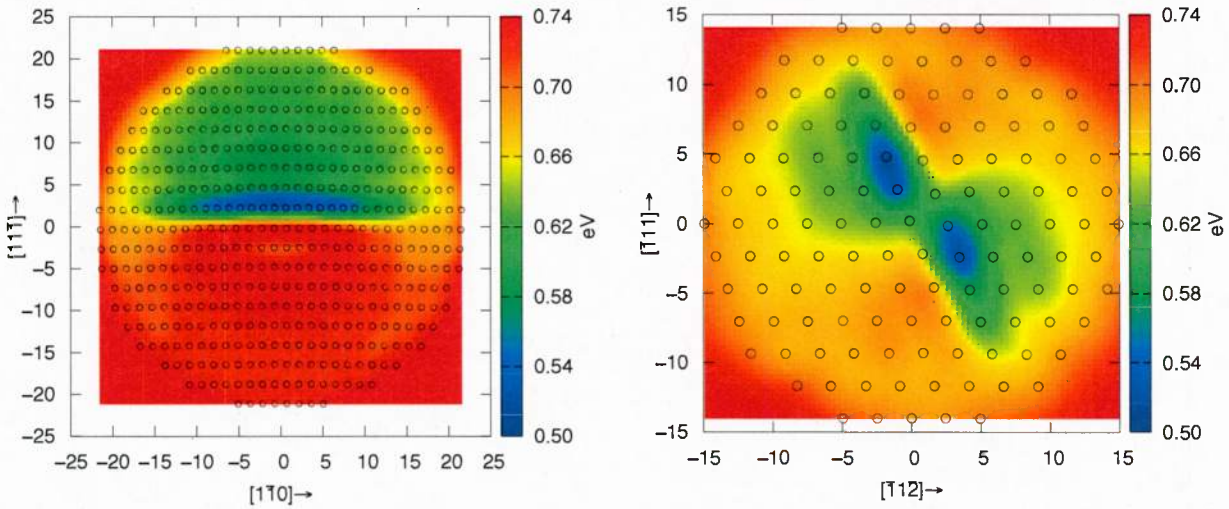

Figure 1: Contour plots of the vacancy formation energy in the core regions of the (a) screw and (b) edge dislocations in Al. The contour interval is 0.02 eV, the innermost contour corresponds to 0.52 eV, and the bulk vacancy formation energy is 0.68 eV. The circles label atomic rows viewed along a <110> direction normal to the page. Note that both dislocations are slightly dissociated into Shockley partials on {111} planes.

To determine the diffusion coefficients D_d, a new method developed in tjos project was applied. Specifically, MD simulations have been run at several temperatures for both dislocations. At each temperature, D_d was obtained from the Einstein equation using mean-squared atomic displacements within the dislocation core averaged over a few nanoseconds. Figure 2 shows typical plots of the mean-squared displacements versus time, demonstrating that the Einstein relation is followed accurately. The diffusion coefficients were obtained from the slopes of such plots. Each calculation is repeated for a dislocation core with a pre-existing single vacancy, with a pre-existing single interstitial, as well as without any point defects. The coefficients computed in the presence of vacancies and interstitials are corrected for the corresponding equilibrium point-defect concentration in the simulation block, using a statistical-mechanical model developed in this project.

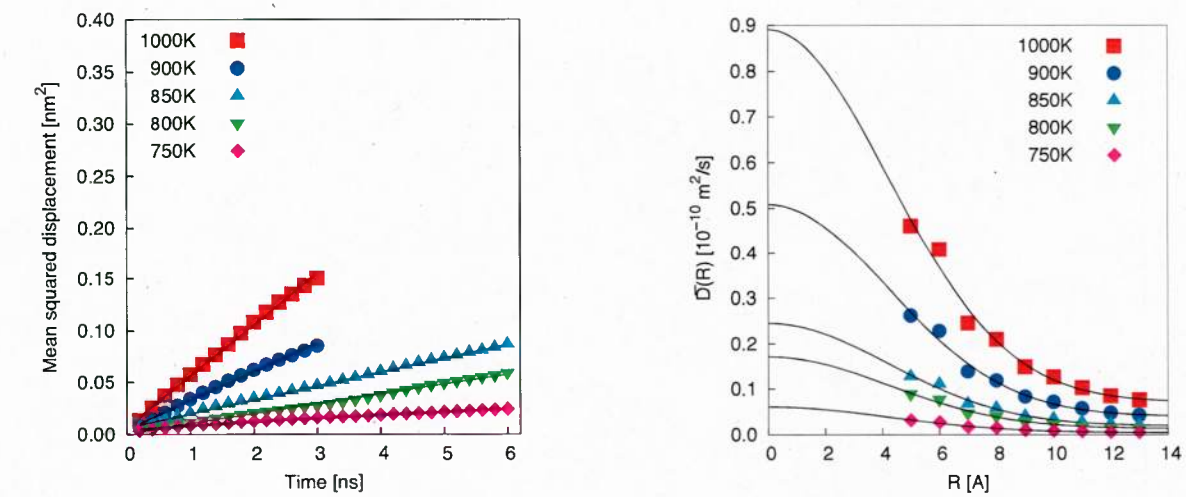

Figure 2: Left: Typical plots of mean-squared atomic displacements in the core of the screw dislocation in Al as a function of time at selected temperatures. The linearity of the plots confirmes that the atoms migrate by a random walk mechanism. The slopes of the lines permit the calculation of the dislocation diffusion coefficient D_d from the Einstein equation. Right: The average core diffusivity as a function of the radius R of the sampling cylinder. Gaussian fits to such plots permit the extraction of the core diffusion coefficient and the effective core radius from the simulation results.

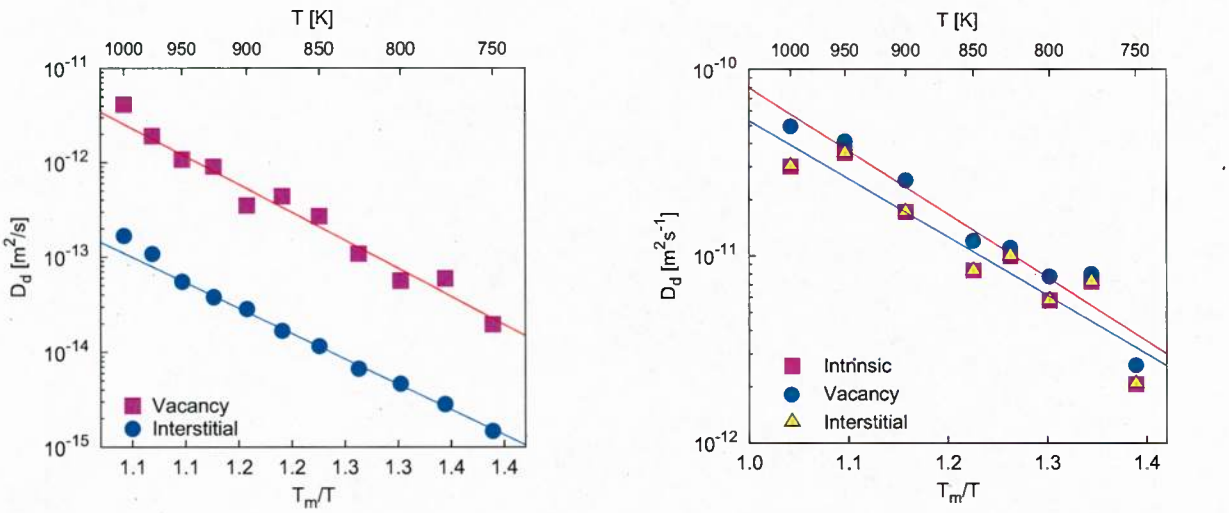

Figure 3: Arrhenius diagrams of diffusion coefficients along (a) screw and (b) edge dislocations in Al in the presence of vacancies, in the presence of interstitials, and without any point defects (intrinsic diffusion). The lines show Arrhenius fits to the data. The temperature is normalized by the melting point T_m.

The Arrhenius diagrams of the calculated diffusion coefficients (Fig. 3) indicate that diffusion along the screw dislocation is faster than along the edge for both vacancies and interstitials. Diffusion in the presence of vacancies is significantly faster than diffusion in the pres-

ence of interstitials. Although the migration barrier for interstitial diffusion is low, the interstitial formation energy even within the dislocation core is so large that their contribution to the overall atomic transport is extremely small. The activation energies of dislocation diffusion deduced from the calculations are in good agreement with experimental data.

The most interesting and unexpected finding of this work is that the dislocation diffusion can occur even in the absence of any point defects in the dislocation core. In fact, at least for the screw dislocation, this "intrinsic" diffusion is faster than the contributions of both vacancies and interstitials. In the edge dislocation, the intrinsic diffusion is only significant at high temperatures, while low temperatures are dominated by either vacancies or interstitials.

The finding that diffusion along screw dislocations is relatively fast and does not require pre-existing points defects is new and important. It may have significant implications for the existing models of many diffusion-controlled processes in metallic materials, including the dynamic strain ageing. In particular, the models based on the notion of vacancy over-saturation or starvation as a factor of dislocation-controlled kinetics may need to be critically reconsidered.

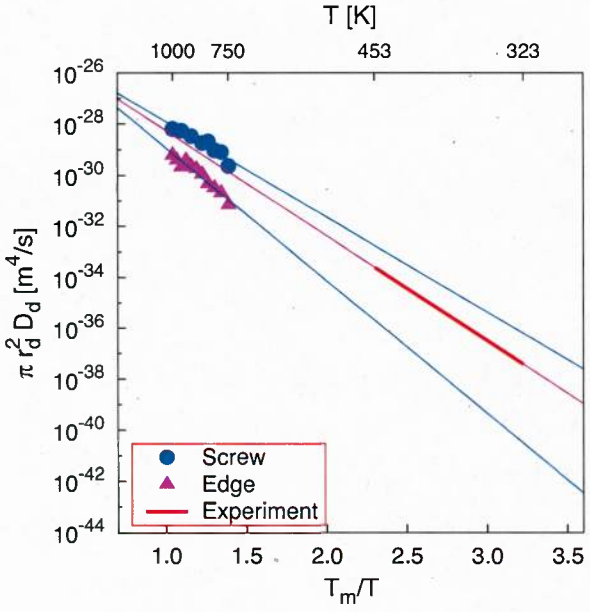

Figure 4: Comparison of calculated experimental data for dislocation core diffusion in Al.

Figure 4 compares our calculations results with indirect experimental measurements based on the void shrinkage kinetics in Al thin films. Because the experimental measurements were made at temperatures much lower than the simulations, we had to extrapolate them to high temperatures. In addition, experiments give access only to the product P the core diffusion coefficient D_d and the effective core radius r_d. We thus had to convert our data to P value to allow comparison. Fig. 4 show that the experimental Arrhenius line extrapolated to our temperature interval is in very good agreement with the simulations. Furthermore, the extrapolation yields experimental values intermediate between the calculations for the screw and edge

dislocations. This is very encouraging since the experiments represent diffusivities of "average" dislocations and it is expected that they will be intermediate between the extreme cases of the screw and edge dislocations.

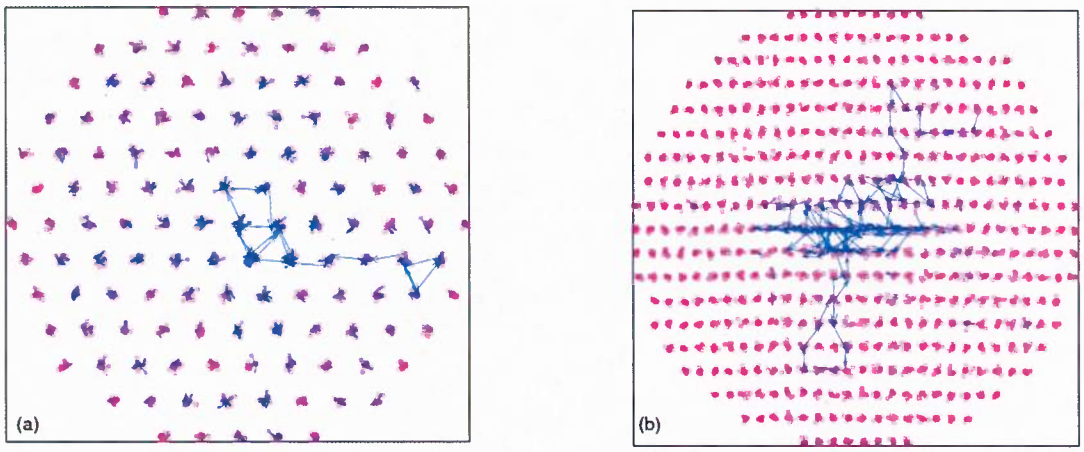

Figure 5: Atomic trajectories showing vacancy migration paths around (a) screw dislocation in Al at 950 K and (b) edge dislocation at 1000 K. The arrows show atomic displacements over a 0.2 nanosecond time interval. The chains of such displacements are signatures of vacancy excursions. The dislocation line is parallel to <110> and normal to the page. Only a part of the simulation block centered at the dislocation line is shown in these plots.

We have put significant efforts to understand the atomic mechanisms of the intrinsic dislocation diffusion by careful examination of numerous MD snapshots and atomic trajectories. Two important observations have been made. Firstly, we find that even in the absence of external point defects, the dislocation core once in a while ejects a single vacancy into the surrounding lattice (Fig. 5). The vacancy makes a short excursion around the core and gets absorbed by it. The frequency of such ejections and duration of the vacancy excursion depends on the temperature. As the vacancy is ejected into the lattice, it must leave an interstitial behind, so that the two defects can be considered as a dissociated Frenkel pair. As they move, they intermix the atoms and thus produce self-diffusion.

Secondly, the screw dislocation line does not remain perfectly straight. Instead, it constantly develops thermal double-jogs of an elementary height (Fig. 6). They spread over the dislocation line and eventually annihilate with their images as new double-jogs appear by thermal fluctuations. As a result, the dislocation is constantly wandering around its average position imposed by the boundary conditions. We observe that this random walk of the dislocation line produces random displacements of atoms and results in their diffusion. In the edge dislocation, the double-jogs are only seen at high temperatures, suggesting that their formation energy is higher than in the screw dislocation.

Based in these observations, the following picture of the intrinsic diffusion has emerged. Even in the absence of pre-existing point defects, the dislocation core can develop Frenkel pairs (vacancy-interstitial) due to thermal fluctuations. Such pairs are likely to be short-lived and quickly annihilate, but even this short live could be enough for producing significant diffusive motion of atoms. In a straight dislocation, the nucleation barrier of Frenkel-pair formation is high and their contribution to diffusion negligibly small. The double-jog formation and spreading assist the nucleation process of the dynamic Frenkel pairs and make their concentration high enough to control the overall diffusion process. The vacancy of the Frenkel pair has a finite probability of jumping out of the core into the surrounding lattice regions. The attractive forces drive the vacancy back into the core, where it reunites with its own or another interstitial. This gives rise to the vacancy excursions which we see in the MD simulations. The relative easiness of the double-jog formation in the screw core explains the greater contribution of the intrinsic diffusion mechanism in comparison with the edge dislocation.

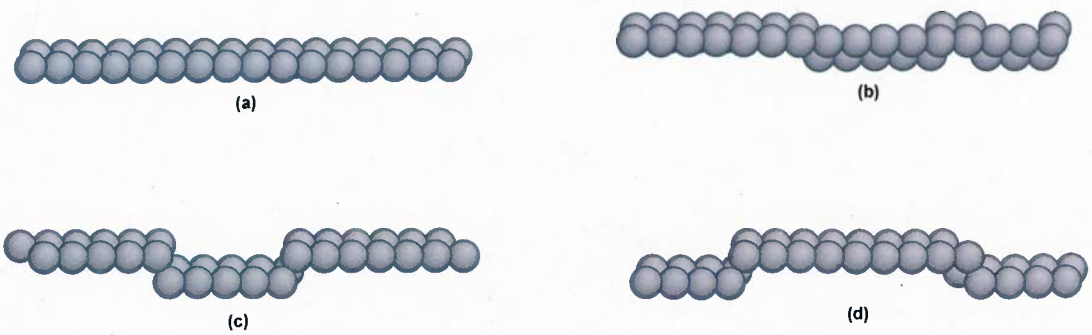

Figure 6: Typical configurations of the screw dislocation line in Al during MD simulations at 750 K. (a) straight dislocation, (b)-(d) dislocation with double-jogs. The spheres show atoms with excess potential energy, which decorate the dislocation core. The horizontal alignment of the two layers of atoms reflects the slight dissociation into Shockley partials.

We have studied atomic diffusion along single dislocations and dislocation networks with the goal of understanding the diffusion mechanisms and developing new accurate methods of diffusion calculations for aerospace Al-alloys. Our simulations have shown that diffusion along edge and screw dislocations is mediated by both vacancies and interstitials, as well as by a new mechanism discovered in this work ("intrinsic" mechanism). The intrinsic diffusion occurs by spontaneous creation of Frenkel pairs, fast diffusion of the interstitial along the dislocation core, and finally its recombination with another vacancy.

When dislocations are assembled into networks in low-angle tilt or twist boundaries, the same mechanisms continue to operate, including the intrinsic mechanism. Diffusion rates along dislocation networks are faster than for isolated dislocations. The diffusion coefficients computed by

molecular dynamics are in excellent agreement with experimental data for Al, confirming the correctness of our methodology.

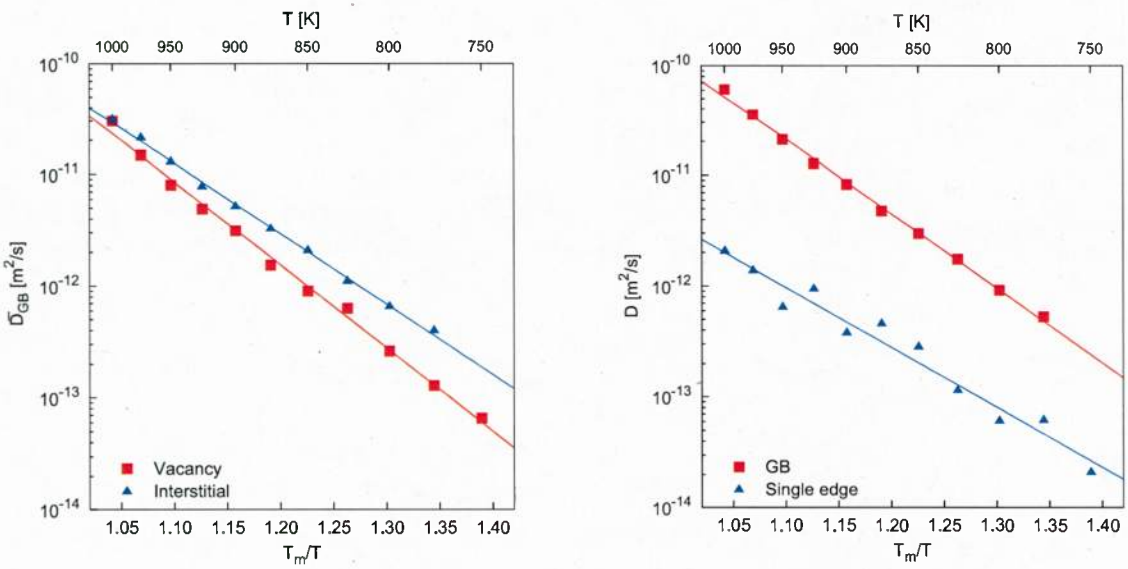

Figure 7: Arrhenius plots of diffusivity in the low-angle tilt grain boundary. Left: Comparison of diffusion coefficients by the vacancy and interstitial mechanisms, showing the predominance of the interstitial mechanism. (b) Comparison of the diffusivities in a single edge dislocation and a low-angle grain boundary composed of edge dislocations, showing the enhanced diffusion due to the collective effect.

Summary of the project

The project goal was to study atomic diffusion along dislocations and their networks and develop new accurate methods of diffusion calculations for aerospace Al-alloys. We have studied self-diffusion along pure screw and edge dislocations in Al using MD simulations with an embedded-atom potential. Diffusion along the screw dislocation is faster than along the edge for both the vacancy and interstitial mechanisms. The most important and unexpected finding is that dislocation diffusion can occur even in the absence of preexisting point defects in the dislocation core. In fact, for the screw dislocation this "intrinsic" diffusion is faster than the contributions of both vacancies and interstitials. This finding may have significant implications for the existing models of many diffusion-controlled processes in metallic materials, including the dynamic strain aging. We have studied diffusion in dislocations assembled into low-angle tilt or twist boundaries. It has been confirmed that the atomic mechanisms that operate are similar to diffusion mechanisms in single dislocations, including the new intrinsic mechanism. Diffusion rates along dislocation networks are a factor of 2 to 3 faster than for isolated dislocations, depending on the temperature. The predicted diffusion coefficients are in excellent agreement with experimental data. The new methodology of dislocation diffusion coefficients is fully transferable and can be allied to study other materials that present interest for Air Force applications.

Publications:

- G. P. Purja Pun and Y. Mishin: Self-diffusion in the core of a screw dislocation in Al, *Defects and Diffusion*, 2007, vol. 266, pp. 49-62.
- G. P. Purja Pun and Y. Mishin: A molecular dynamics study of self-diffusion in the cores of screw and edge dislocations in aluminum, *Acta Materialia*, 2009, vol. 57, pp. 5531-5542.
- G. P. Purja Pun and Y. Mishin: Diffusion mechanisms in low-angle grain boundaries in Al, *Acta Materialia*, 2010, submitted for publication.

Personnel supported

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Acknowledgemen/Displaimer

This work was sponsored by the Air Force Office of Scientific Research, USAF, under grant number FA9550-07-1-0240. The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied, of the Air Force Office of Scientific Research or the U.S. Government.